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NITROGEN REMOVAL BY BREAKPOINT CHLORINATION

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Cincinnati, Ohio

September 1970

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ABSTRACT

Sodium hypochlorite was used to oxidize the ammonia in buffered distilled water systems and in raw, secondary and lime clarified municipal wastewaters. In systems with only ammonia as the chlorine demand, the breakpoint exhibited a minimum chlorine dose at approximately an 8:1 weight ratio of $Cl:NH_3$-N in the pH range of 6-7. End products at the breakpoint were N_2, NCl_3, and NO_3^-. Qualitatively, the formation of the N_2 was completed in less than one minute. At the breakpoint in buffered distilled water with 20 mg/l of NH_3-N, the formation of NO_3^--N decreased from about 2.0 mg/l at pH 8.0 to 0.3 mg/l at pH 5-6. NCl_3-N formation in the same system at the breakpoint decreased from approximately 0.3 mg/l at pH 5.0 to 0.05 mg/l at pH 8.0. In the pH range of 5-8, less than 0.3 mg/l of NCl_3-N formed before the breakpoint. In wastewater, the breakpoint required a minimum chlorine dose of approximately an 8:1 weight ratio of $Cl:NH_3$-N in lime clarified secondary effluent. The chlorine dosage to achieve the breakpoint increased as the degree of wastewater treatment decreased. The organic nitrogen in the wastewater was not removed within the 2 hour reaction period.

Keywords:

breakpoint chlorination

ammonia removal

nitrogen trichloride formation

nitrate formation

NITROGEN REMOVAL
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BREAKPOINT CHLORINATION*

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Breakpoint chlorination, as practiced for many years in the water treatment industry provides a physical-chemical means for removing ammonia from wastewaters. In water, at NH_3-N concentrations usually below 1 mg/l, chlorine reacts with the ammonia to form various chloramines:

$$(1) \quad Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$(2) \quad NH_4^+ + HOCl \longrightarrow NH_2Cl + H_2O + H^+$$

$$(3) \quad NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$$

$$(4) \quad NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$$

Chlorine is added to process waters until a point is reached where the total dissolved residual chlorine has reached a minimum (the breakpoint) and the NH_3-N has disappeared.

In water at NH_3-N concentrations of less than 1 mg/l, and before the breakpoint, the type of chloramine formed depends upon the pH. Spectrophotometric analyses [2, 4, 5, 12, 14] indicates that the chief constituent is monochloramine in the pH range of 7-8.5. As the pH decreases below 7, increasing amounts of dichloramine appear. In the pH range of

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4.5-5.0, dichloramine is the chief product; below pH 4, nitrogen trichloride is the chief product.

Breakpoint chlorination studies [17] on buffered synthetic ammonia samples at pH 7.0 reveal that monochloramine concentration reaches a maximum at the 5:1 weight ratio of $Cl:NH_3$-N. As the weight ratio of $Cl:NH_3$-N exceeds 5:1, the monochloramine breaks down [6] to form dichloramine and ammonia (equation 5).

$$(5)\quad 2NH_2Cl \longrightarrow NHCl_2 + NH_3$$

The dichloramine reaches a maximum concentration at the $Cl:NH_3$-N weight ratio of about 7.5:1.

The literature [7] indicates that in water with less than 1 mg/l of NH_3-N, the reaction proceeds in competition with monochloramine formation (equation 2) until the chlorine dosage reaches the breakpoint at approximately a 10:1 weight ratio of $Cl:NH_3$-N. Other studies, [3,14] however, indicate that monochloramine is oxidized by excess chlorine under slightly alkaline conditions to nitrogen gas (equation 6).

$$(6)\quad 2NH_2Cl + HOCl \longrightarrow N_2 + 3HCl + H_2O$$

Stoichiometrically, the ammonia oxidation through monochloramine to N_2 corresponds to a 7.6:1 weight ratio of $Cl:NH_3$-N. The literature [2,4,7,14] also suggests the occurrence of other end-products, including nitrate and nitrogen trichloride. In fact, the nitrogen trichloride produced (equation 4) in water treatment plants [10] during breakpoint chlorination has been a serious problem.

In wastewaters, the NH_3-N concentration may be more than an order of

magnitude higher than those normally encountered in natural waters. For use of breakpoint chlorination for nitrogen removal at the NH_3-N concentrations encountered in wastewaters, the end products of the reaction need to be known. This study identified the major products of the breakpoint reaction in synthetic buffered solutions and in wastewaters and determines the formation and behavior of the nuisance residuals of NCl_3 and NO_3^- as a function of pH, chlorine dosage, and temperature.

EXPERIMENTAL

The chlorination studies were performed in synthetic buffered systems, usually with initial NH_3-N concentrations of 20 mg/l, to eliminate effects from other substances reacting with chlorine and in raw, secondary, and lime clarified municipal wastewaters with NH_3-N concentrations ranging from 8-15 mg/l.

In end product identification studies on buffered aqueous systems, the gaseous products were qualitatively analyzed for N_2, O_2, and N_2O. The procedure involved purging the aqueous sample containing 20 mg/l NH_3-N and buffered at pH 7.5 with helium to remove atmospheric nitrogen in a closed system attached to a gas chromatograph. The sample was then treated with nitrogen-free standard sodium hypochlorite at a dosage equal to a 10:1 weight ratio of $Cl:NH_3$-N. The gaseous products of the reaction were then flushed through the gas chromatograph with helium.

A test was also performed to identify the presence of any nitric oxide (NO) or nitrogen dioxide (NO_2). An enclosed breakpoint chlorinated sample was purged with air into a cold solution of .02N H_2SO_4 to remove any NO or NO_2 formed during the chlorination. In the procedure, [13] the

NO was oxidized to NO_2 by the oxygen in the air and absorbed in the .02N H_2SO_4 as nitrous and nitric acids. The .02N H_2SO_4 solution was then analyzed for $(NO_3^- + NO_2^-)$-N.

Spectrophotometric scanning of both chlorinated aqueous samples and their CCl_4 extracts was also performed to determine other end-products. The samples, after two hours of contact with the chlorine, were placed in a recording spectrophotometer and scanned over the spectral range of 200-500 mμ.

In the quantitative studies, aqueous ammonia or wastewaters samples were manually mixed in separatory funnels with increasing dosages of standard sodium hypochlorite over the pH range of 5-8. A two-hour contact time [17] was provided for all systems. The samples, after chlorination, were analyzed for $(NO_3^- + NO_2^-)$-N, NCl_3-N, NH_3-N, NH_2Cl and $NHCl_2$-N, TK-N, total residual chlorine, free available chlorine and pH.

Quantitative temperature studies were also conducted at 5,15,25, and 40^oC on aqueous ammonia samples containing 20 mg/l NH_3-N and buffered at pH 6.0 to determine temperature effects on the end-products. Multiple samples in separatory funnels were cooled to the designated temperature in a constant temperature bath and treated with increasing dosages of pre-cooled sodium hypochlorite. The samples were then manually mixed and allowed to stand at the selected temperature for two hours before analysis.

ANALYTICAL PROCEDURES

A modified automated hydrazine reduction method [9] with an alkaline digestion to eliminate chloramine interferences was developed for the $(NO_3^- + NO_2^-)$-N analysis. In this procedure, the sample was made alkaline

with NaOH, digested to dryness, redissolved and neutralized with HCl and diluted to volume for analysis. This modified procedure was reliable to ± .05 mg/l NO_3^--N.

Nitrogen trichloride was analyzed according to the spectrophotometric procedure of Czeh et al. [5] in the synthetic ammonia samples and in wastewater samples by both the spectrophotometric procedure of Czeh et al. and the Modified Palin Method. [16] The results of spectrophotometric analysis of NCl_3 on wastewater samples were reproducible to ± .05 mg/l NCl_3-N. While analyses from the Palin Method were similar to those from the spectrophotometric procedure, they were poorly reproducible; therefore, the analyses from the spectrophotometric procedure were employed in the evaluation of the breakpoint studies on wastewaters. The spectrophotometric procedure for the analysis of NCl_3, however, represented all compounds extracted from the wastewater that absorb at 265 and 345 mμ in CCl_4.

Free available chlorine, mono and di-chloramine were analyzed according to the Modified Palin Method [16] with N, N-diethyl-p-phenylenediamine oxalate as the indicator, and by amperometric titration. [15] All other analyses employed the procedures of "Standard Methods for the Examination of Water and Wastewaters". [15]

A Varian Aerograph Gas Chromatograph (Model 1532-2B) equipped with an ionization detector (with a tritium source) and a molecular sieve type column, designed to detect N_2, O_2, and N_2O, was used to qualitatively analyze the gaseous product. A Forma (Model 2095) circulating-constant temperature bath was used to control the temperature of the studies to ± 0.1°C. U. V. absorbancies were determined on a Beckman DU Spectrophotometer or on a Beckman DBG recording Spectrophotometer, both with 10 mm quartz cells.

The NCl_3 standard was prepared by the method of Noyes [1] and assayed. Aliquots of the stock were diluted in carbon tetrachloride to make standard solutions ranging from 0-100 mg/l NCl_3. The NCl_3 standards scanned in the spectrophotometer produced peaks only at 265 and 345 mμ with linear absorbancies for increasing NCl_3 concentrations. The molar absorptivities calculated from the standards were 228 for the peak at 345 mμ and 445 for the peak at 265 mμ. The molar absorptivities reported by Czeh, Fuchs, and Antczak [5] were 232 for the peak at 345 mμ and 450 for the peak at 265 mμ.

Spectrograde CCl_4 was used throughout the study for extraction and dilution of standard and unknown samples. All other reagents used in the study were of reagent quality.

END PRODUCTS

In buffered solutions at pH 7.5 with 20 mg/l NH_3-N, gas chromatographic analysis for N_2, O_2, and N_2O at the breakpoint detected only N_2. Since O_2 was not detected, the formation of N_2O with subsequent decomposition to N_2 and O_2 did not occur. Qualitatively, the formation of the N_2 was completed in less than one minute. The tests for nitric oxide (NO) and nitrogen dioxide (NO_2) revealed that neither of these compounds were present.

Spectrophotometric scans (200-500 mμ) of the buffered solution treated with increasing dosages of chlorine up to Cl:NH_3-N weight ratio of 7.5:1 revealed adsorption peaks at 243 mμ for monochloramine [11] and at 205 mμ for nitrate; [15] above the 7.5:1 ratio the peak at 243 mμ disappeared and a peak at 287 mμ appeared and increased with increasing chlorine doses. The control sample containing only the buffered solution

with free chlorine and without NH_3-N, produced a peak only at 287 mμ. Thus, the peak at 287 mμ above the 7.5:1 ratio of $Cl:NH_3$-N was produced by free chlorine.

The absorbance produced by monochloramine at 243 mμ increased linearly with increasing chlorine dosages to a maximum at the 5:1 weight ratio of $Cl:NH_3$-N and then decreased to near zero at approximately the 7.6:1 ratio. The strong peak produced by NO_3^- at 205 mμ increased with increasing chlorine dosage through the 12:1 weight ratio of $Cl:NH_3$-N and confirmed the formation of NO_3^- during chlorination. In summary, spectral scanning of the aqueous solutions indicated only the formation and decomposition of monochloramine, the gradual formation of NO_3^--N and the presence of free available chlorine after the breakpoint. The CCl_4 extracts, scanned in the spectrophotometer in the range of 200-500 mμ against a reference control blank, produced strong NCl_3 peaks [5] at 265 and 345 mμ only after the chlorine dosage exceeded the 7.5:1 weight ratio of $Cl:NH_3$-N.

pH AND TEMPERATURE

The addition of chlorine to buffered aqueous samples containing 20 mg/l NH_3-N at pH 7.0 produced a typical breakpoint curve with the complete removal of the ammonia and a minimum total residual chlorine concentration of about 0.6 mg/l at approximately 8:1 weight ratio of $Cl:NH_3$-N (Figure 1 and 2). The chlorination studies of buffered solutions at pH 7.0 containing 1 mg/l NH_3-N also reached the breakpoint at approximately an 8:1 weight ratio of $Cl:NH_3$-N. In all tests on buffered aqueous systems in the pH range of 6-7, the breakpoint occurred at chlorine doses approximately equal to an 8:1 (stoichimetric ratio 7.6:1 equations 2 and 6) weight ratio

of $Cl:NH_3$-N. Outside of the 6-7 pH range, the chlorine dose required for the breakpoint increased (Figure 1).

In pH studies on synthetic samples containing 20 mg/l NH_3-N, the formation of NO_3^--N at the breakpoint (Figure 3) increased with increasing pH from about 0.3 mg/l (1.5% of the NH_3-N) at pH 5.0 to about 2.0 mg/l (10% of the NH_3-N) at pH 8.0. With increasing chlorine dosages above the breakpoint, the NO_3^--N formation increased sharply at pH 6.0 and above, but increased only slightly in the pH range of 5-6. Thus, low pH (5-6) produced minimum amounts (0.3 mg/l) of NO_3^--N.

In contrast, the amount of NCl_3-N formed at the breakpoint decreased from approximately 0.3 mg/l (1.5%) at pH 5.0 to 0.05 mg/l (0.25%) at pH 7 or 8 (Figure 4). In the pH range of 7-8, a NCl_3-N concentration of less than 0.1 mg/l occurred at the breakpoint. As chlorine dosages exceeded the breakpoint, the formation of NCl_3 increased sharply at and below pH 7.0. At pH 8.0, however, the NCl_3 concentration increased but never exceeded approximately 0.3 mg/l for chlorine dosages up to a 12:1 weight ratio of $Cl:NH_3$-N. With NCl_3 a greater nuisance potential than nitrate, chlorination at the 9:1 weight ratio of $Cl:NH_3$-N (slightly above the breakpoint) minimized NCl_3 residuals at pH 8 but maximized nitrate formation (Figure 5).

The 0.05 mg/l of NCl_3 at the breakpoint (produced by the oxidation of dichloramine) [6] also indicated only small amounts of dichloramine formed above pH 7. The modified Palin Analysis for dichloramine revealed less than 0.1 mg/l $NHCl_2$-N above pH 7 after 2 hours of contact time for all chlorine dosages.

Breakpoint chlorination studies on buffered aqueous systems at pH 6.0 were conducted in the temperature range of 5-40°C. These tests did not

reveal significant changes in the reaction products after the 2 hour contact time. Complete removal of the NH_3-N was achieved at all temperatures (Table 1).

CHLORINATION OF WASTEWATERS

In breakpointing of unclarified and lime clarified raw and secondary wastewaters (NH_3-N concentrations of 8-15 mg/l) with sodium hypochlorite, the $CaCO_3$ alkalinities of 80-120 mg/l in the water maintained the pH of all the samples between 6.5 and 7.5. The chlorine demand required for the breakpoint decreased and approached the stoichiometric amount (equation 2 and 6) for oxidation of NH_3 to N_2 as the degree of wastewater pretreatment increased. As an example, a chlorine dosage equivalent to a 10:1 weight ratio of Cl:NH_3-N was required to breakpoint raw wastewater (Figure 6), while a 9:1 weight ratio was required in the secondary effluent (Figure 10), and less than an 8:1 weight ratio of Cl:NH_3-N for lime clarified and filtered secondary effluent (Figure 12).

If chlorine is employed rather than sodium hypochlorite, the breakpoint chlorination of ammonia concentrations normally encountered in wastewaters may produce more acid than can be neutralized by the buffer capacity of the wastewater. Stoichiometrically (equation 1 and 6) 14.28 mg/l of $CaCO_3$ alkalinity are required to neutralize the acid produced by the oxidation of one mg/l NH_3-N to N_2. Therefore, a wastewater containing 20 mg/l NH_3-N requires an alkalinity of about 286 mg/l. Since the amount of NCl_3 formed before the breakpoint increases with decreasing pH, any excess acid produced must be neutralized with proper mixing to avoid both excess local chlorine concentrations and low pH. Thus if a lime clarified secondary wastewater

contained 20 mg/l NH_3-N, approximately 160 mg/l of chlorine would be required for breakpoint chlorination. At chlorine costs of $C.04/lb., the chlorine cost would be $0.05 per 1000 gallons of treated water. The variable cost of neutralizing excess acid in a specific wastewater and other handling costs must be added to the chlorine cost.

Total kjeldahl nitrogen analyses revealed near complete removal of the NH_3-N, but only a slight reduction of the organic nitrogen within the two hour contact time (Figures 6, 8, 10, 12). The nuisance residuals of nitrate and nitrogen trichloride-nitrogen at the breakpoint were always less than 1 mg/l (Figures 7, 9, 11, 13). The formation of NCl_3 decreased with decreasing wastewater pretreatment, and did not occur in the raw wastewater.

CONCLUSIONS

Breakpoint chlorination in buffered aqueous solutions of 20 mg/l of NH_3-N in the pH range of 5.0-8.0 oxidized the ammonia chiefly to N_2 with only small amounts of NO_3^- and NCl_3 also formed. During chlorination, monochloramine concentrations increased with chlorine dose through about a 5:1 weight ratio of $Cl:NH_3$-N and then decreased to zero at the breakpoint. Only traces of $NHCl_2$ occurred in the 5-8.0 pH range with less than 0.1 mg/l above pH 7. Potential products of N_2O, O_2 (from the decomposition of N_2O), NO and NO_2 did not occur. The minimum chlorine dosage for the breakpoint of less than 8.1 weight ratio of $Cl:NH_3$-N occurred in the range of pH 6 to 7.

The amount of NO_3^- produced at the breakpoint increased from about 1.5% of the NH_3-N at pH 5 to about 10% at pH 8.0 in the aqueous systems. In contrast, the NCl_3 production at the breakpoint decreased from approximately

1.5% of the NH_3-N at pH 5 to .25% at pH 8.0. In the 2 hour contact time of the study, breakpointing at temperatures of 5^o- 40^o did not change the amounts of the products or the required chlorine dose.

In the pH range of 6.5-7.5, breakpoint chlorination of ammonia in wastewaters oxidized 95-99% of the ammonia to nitrogen gas and chemically achieved the results of the natural biochemical nitrogen cycle. When chlorine demands other than ammonia were minimized by pretreatment (lime clarified secondary effluent), the chlorine dosages (8:1 weight ratio of $Cl:NH_3$-N) required for the breakpoint approached the stoichiometric (7.6:1 weight ratio) dosage to oxidize ammonia to N_2. Residuals of NO_3^- and NCl_3 were also formed in the wastewaters but with initial NH_3-N concentrations of 8-15 mg/l, the NO_3^--N residuals never exceeded 0.5 mg/l at the breakpoint; and the NCl_3-N residual never exceeded 0.5 mg/l.

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TABLE 1

Breakpoint Chlorination
Temperature Studies

Temp.	Cl:N wt. ratio	NH_3-N mg/l	NO_3^- + NO_2^--N mg/l	NCl_3-N mg/l
5°C	0	20.0	0.00	0.00
	5:1	9.20	0.10	0.00
	6:1	6.10	0.18	0.00
	7:1	1.19	0.27	0.00
	8:1	0.00	0.43	1.10
	9:1	0.00	0.50	1.89
	10:1	0.00	0.60	3.91
	11:1	0.00	0.70	5.67
15°C	0	20.0	0.00	0.00
	5:1	9.69	0.05	0.00
	6:1	6.00	0.05	0.00
	7:1	1.22	0.16	0.00
	8:1	0.00	0.30	1.10
	9:1	0.00	0.43	1.90
	10:1	0.00	0.52	3.90
	11:1	0.00	0.60	5.67
40°C	0	20.0	0.00	0.00
	5:1	9.20	0.00	0.00
	6:1	6.70	0.10	0.00
	7:1	3.90	0.15	0.00
	8:1	0.00	0.42	1.10
	9:1	0.00	0.47	1.92
	10:1	0.00	0.55	4.00
	11.1	0.00	0.66	5.70

Contact Time = 2 hours
pH 6.0

Figure 1 - CHLORINATION AND pH

Buffered Distilled Water; NH_3-N = 20 mg/l; Temp. = 25°C

FIGURE 1

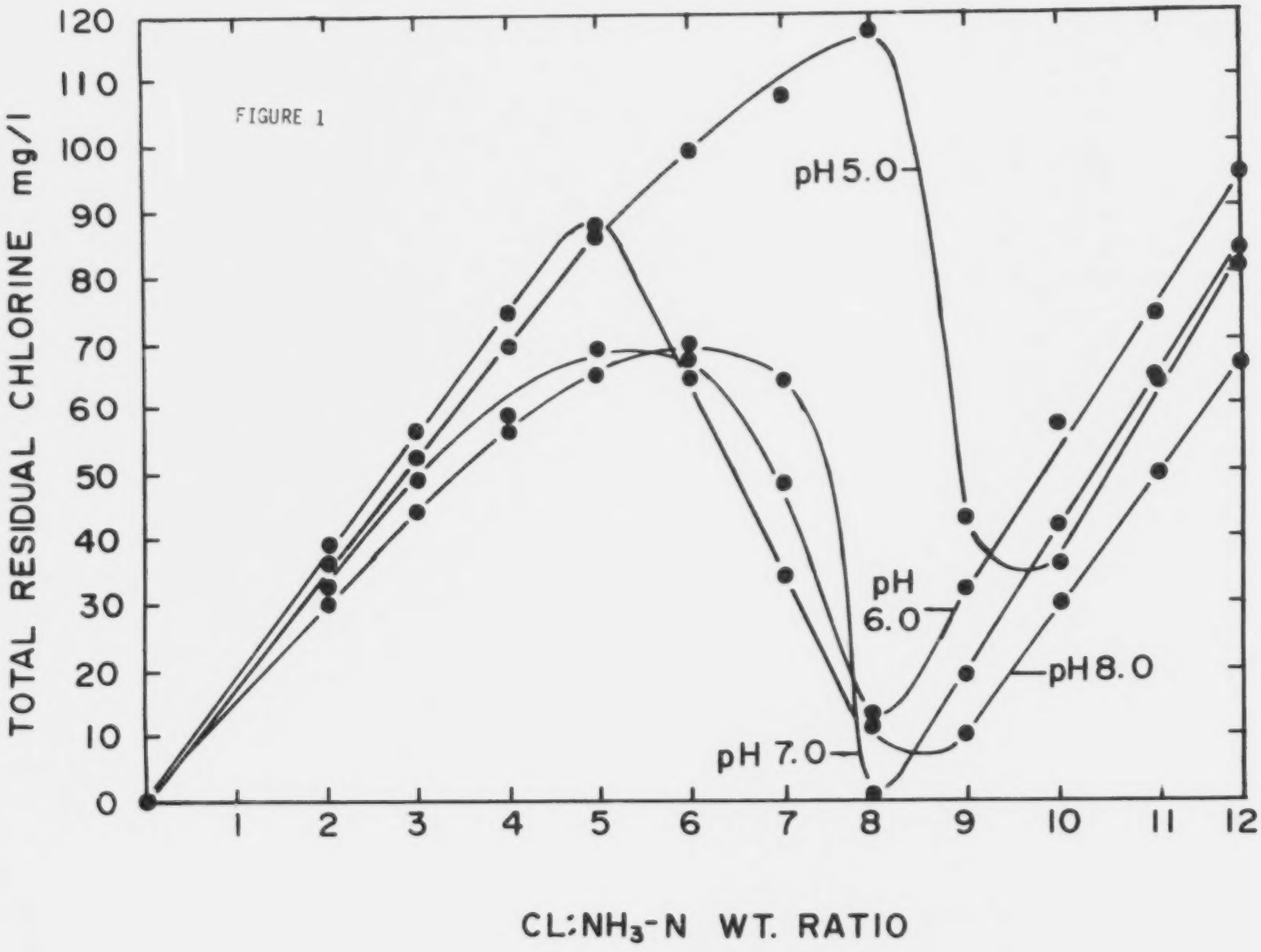
TOTAL RESIDUAL CHLORINE mg/l
0
10
20
30
40
50
60
70
80
90
100
110
120
1
2
3
4
5
6
7
8
9
10
11
12
CL:NH3-N WT. RATIO
pH 5.0
pH 6.0
pH 7.0
pH 8.0

Figure 2 - BREAKPOINT CHLORINATION AND pH

Buffered Distilled Water; NH_3-N = 20 mg/l; Temp. = $25^{o}C$

FIGURE 2

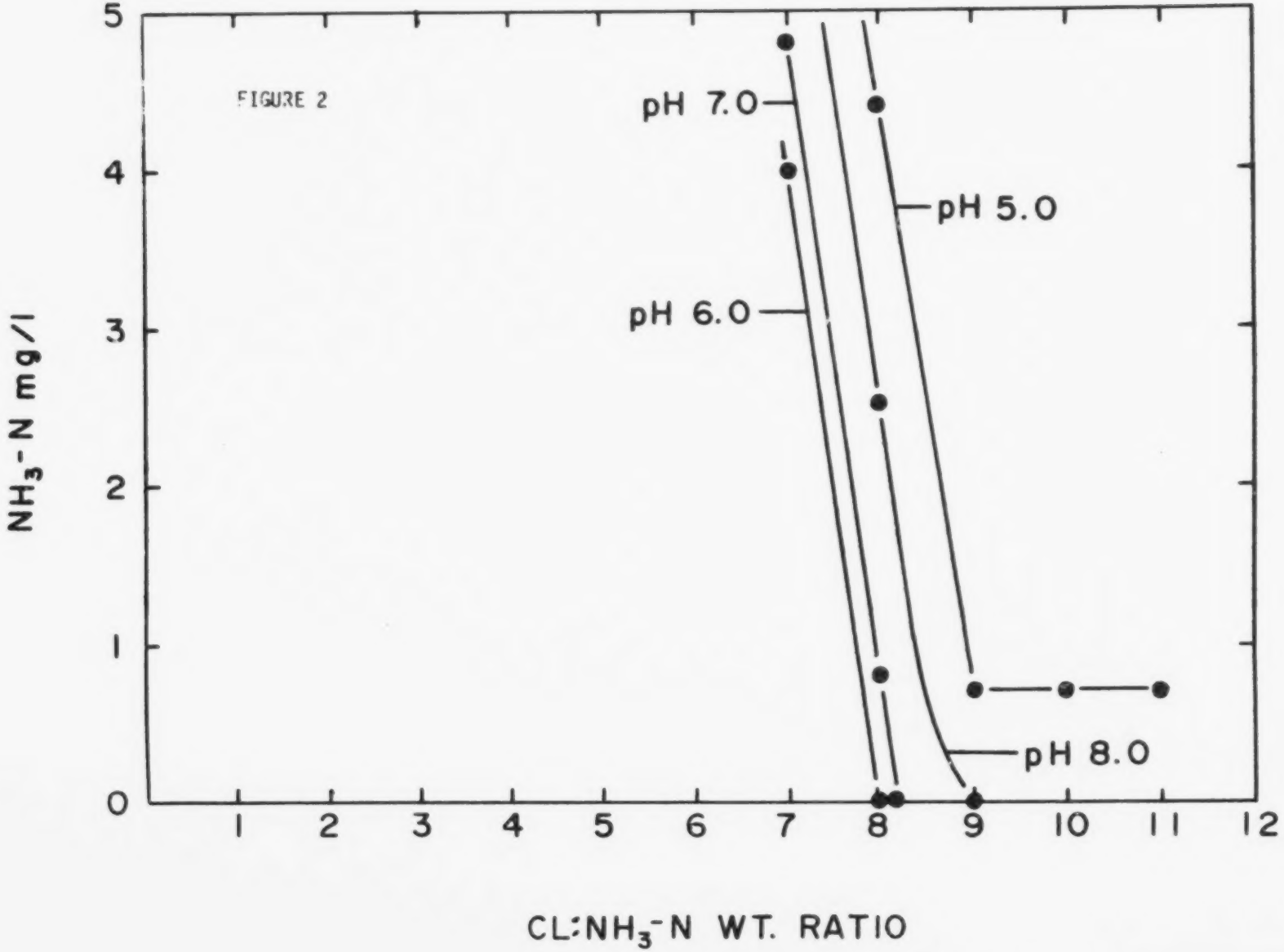
pH 7.0
pH 5.0
pH 6.0
pH 8.0
NH_3-N mg/l
CL:NH_3-N WT. RATIO
0
1
2
3
4
5
6
7
8
9
10
11
12

Figure 3 - NITRATE AND NITRITE FORMATION AND pH

Buffered Distilled Water; NH_3-N = 20 mg/l; Temp. = $25^{o}C$

pH 8.0: Breakpoint between the 8:1 and 9:1 wt. ratio of Cl:NH_3-N

pH 7.0: Breakpoint at approximately 8:1 wt. ratio of Cl:NH_3-N

pH 6.0: Breakpoint at approximately 8:1 wt. ratio of Cl:NH_3-N

pH 5.0: Breakpoint between the 9:1 and 10:1 wt. ratio of Cl:NH_3-N

FIGURE 3

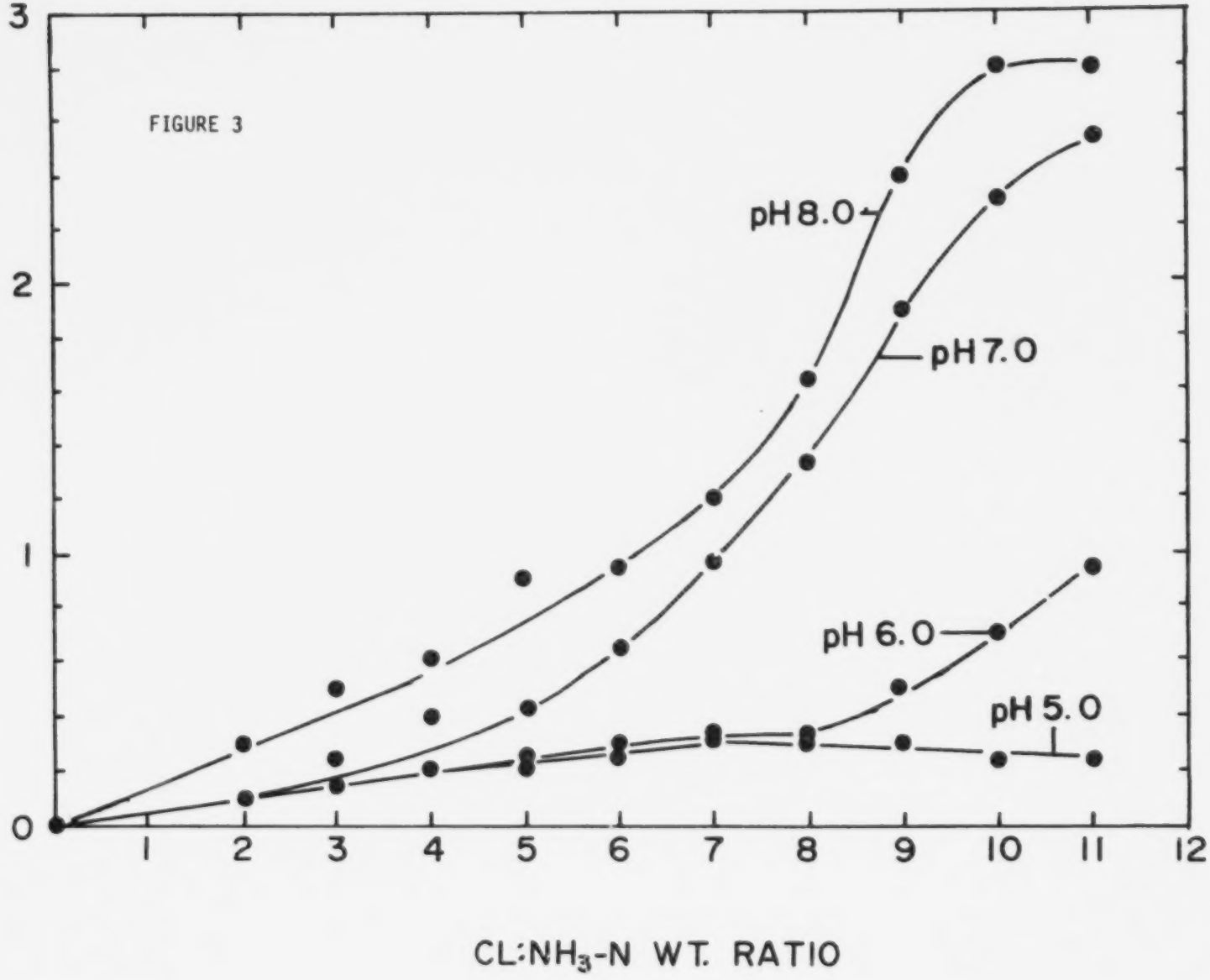
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
12
pH 8.0
pH 7.0
pH 6.0
pH 5.0
$NO_3^- + NO_2^-$-N mg/l
CL:NH_3-N WT. RATIO

Figure 4 - NITROGEN TRICHLORIDE FORMATION AND pH

Buffered Distilled Water; NH_3-N = 20 mg/l; Temp. = 25°C
pH 8.0: Breakpoint between the 8:1 and 9:1 wt. ratio of Cl:NH_3-N
pH 7.0: Breakpoint at approximately 8:1 wt. ratio of Cl:NH_3-N
pH 6.0: Breakpoint at approximately 8:1 wt. ratio of Cl:NH_3-N
pH 5.0: Breakpoint between the 9:1 and 10:1 wt. ratio of Cl:NH_3-N

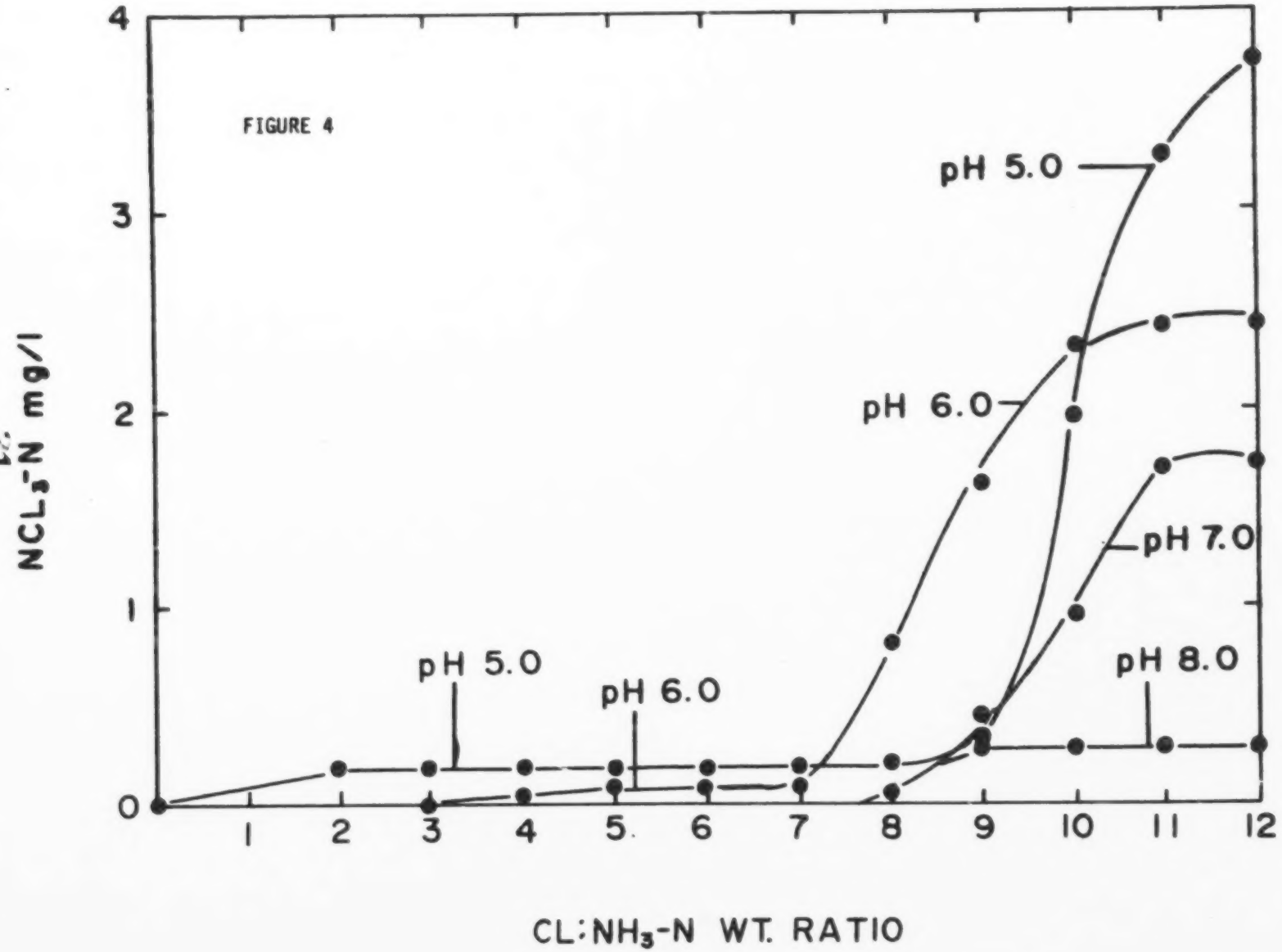
FIGURE 4
pH 5.0
pH 6.0
pH 7.0
pH 8.0
pH 5.0
pH 6.0
0
1
2
3
4
1
2
3
4
5
6
7
8
9
10
11
12
NCL:NH3-N mg/l
CL:NH3-N WT. RATIO

Figure 5 - NITROGEN TRICHLORIDE AND NITRATE + NITRITE

Formation Versus pH. 9:1 Weight Ratio of Cl: NH_3-N

(Above Breakpoint)

Buffered Distilled Water; NH_3-N = 20 mg/l; Temp. = 25^oC

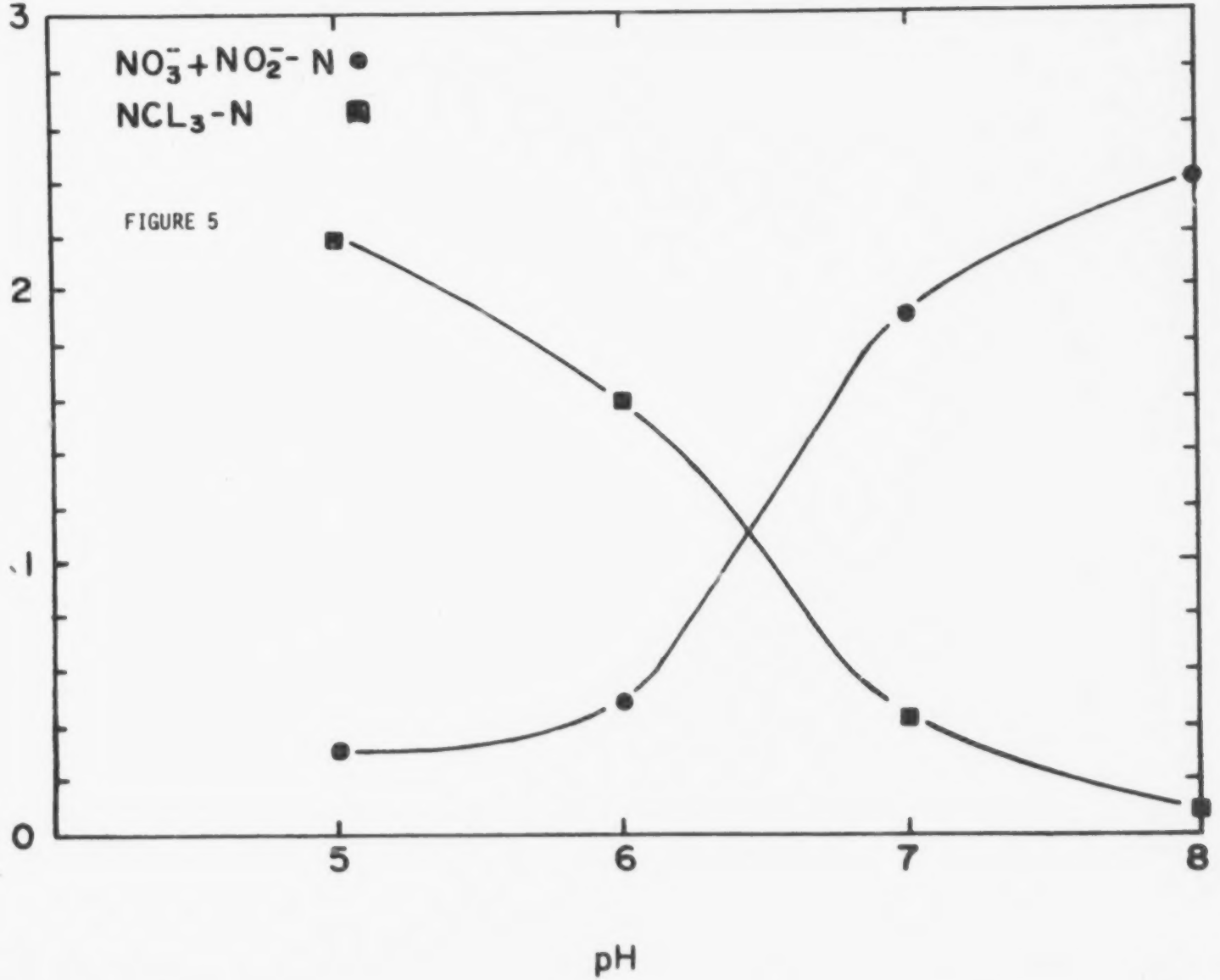

FIGURE 5

Figure 6 - CHLORINATION OF RAW WASTEWATER

Temperature = 23°C; NH_3-N = 15.0 mg/l; Suspended Solids = 234 mg/l; Total Alkalinity = 120 mg/l $CaCO_3$; pH Range During Chlorination = 6.5 - 7.5; Breakpoint between the 9:1 and 10:1 weight ratio of Cl:NH_3-N.

FIGURE 6

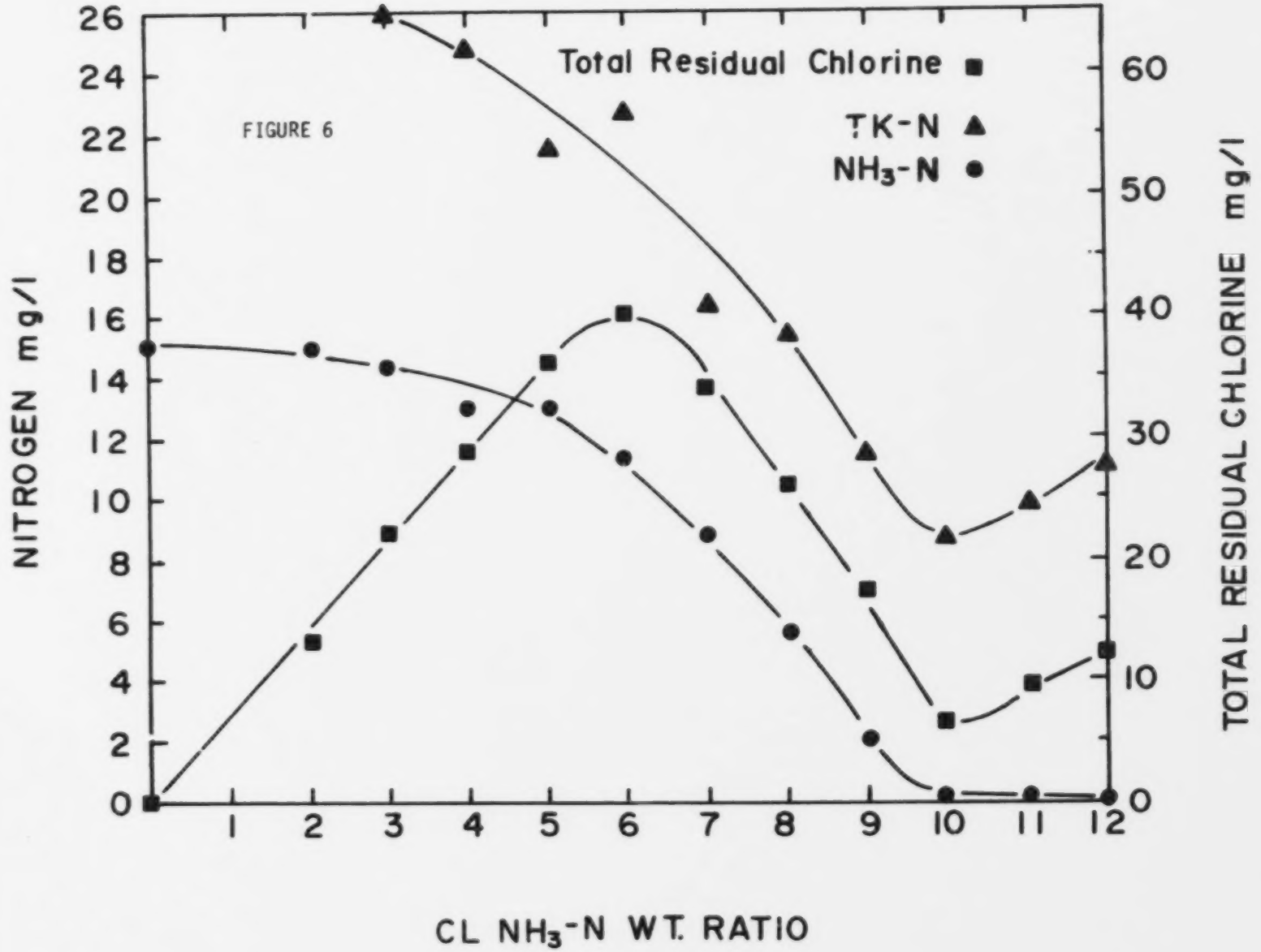
Total Residual Chlorine ■
TK-N ▲
NH3-N ●
NITROGEN mg/l
TOTAL RESIDUAL CHLORINE mg/l
CL NH3-N WT. RATIO
0
2
4
6
8
10
12
14
16
18
20
22
24
26
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8
9
10
11
12

Figure 7 - NITROGEN TRICHLORIDE AND NITRATE FORMATION DURING THE CHLORINATION OF RAW WASTEWATER

Temperature = 23°C; NH_3-N = 15.0 mg/l; Suspended Solids = 234 mg/l; Total Alkalinity = 120 mg/l $CaCO_3$; pH Range During Breakpointing = 6.5 - 7.5; Breakpoint between the 9:1 and 10:1 weight ratio of Cl:NH_3-N.

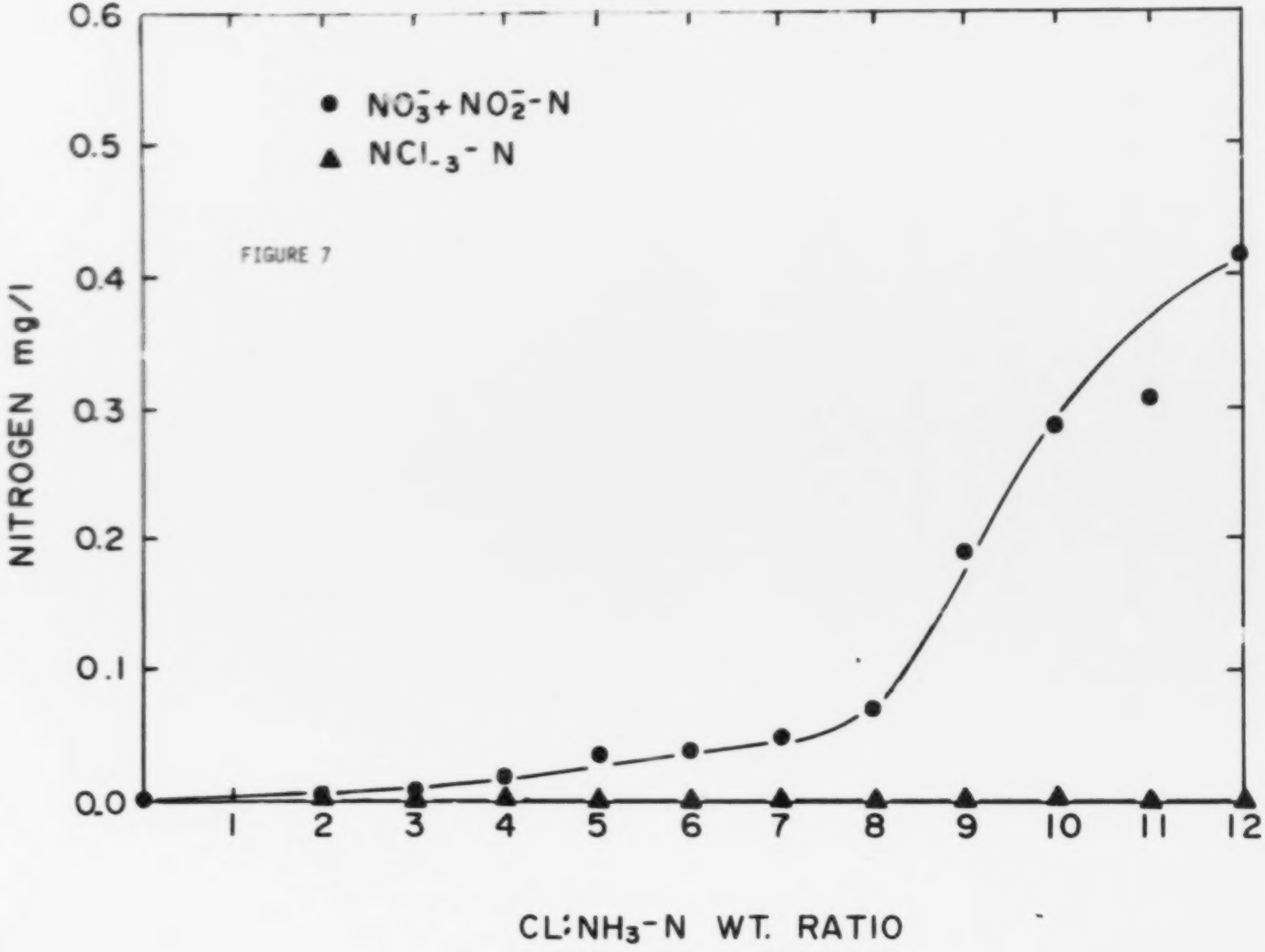
0.6
0.5
0.4
0.3
0.2
0.1
0.0
NITROGEN mg/l
● $NO_3^- + NO_2^-$-N
▲ NCl_3- N
1
2
3
4
5
6
7
8
9
10
11
12
CL:NH_3-N WT. RATIO

FIGURE 7

Figure 8 - CHLORINATION OF LIME CLARIFIED AND FILTERED RAW WASTEWATER

Temperature = 23°C; NH_3-N = 11.2 mg/l; Suspended Solids = 4 mg/l; Total Alkalinity = 84 mg/l $CaCO_3$; pH Range During Chlorination = 6.5 - 7.5; Breakpoint between the 8:1 and 9:1 weight ratio of Cl:NH_3-N.

FIGURE 8

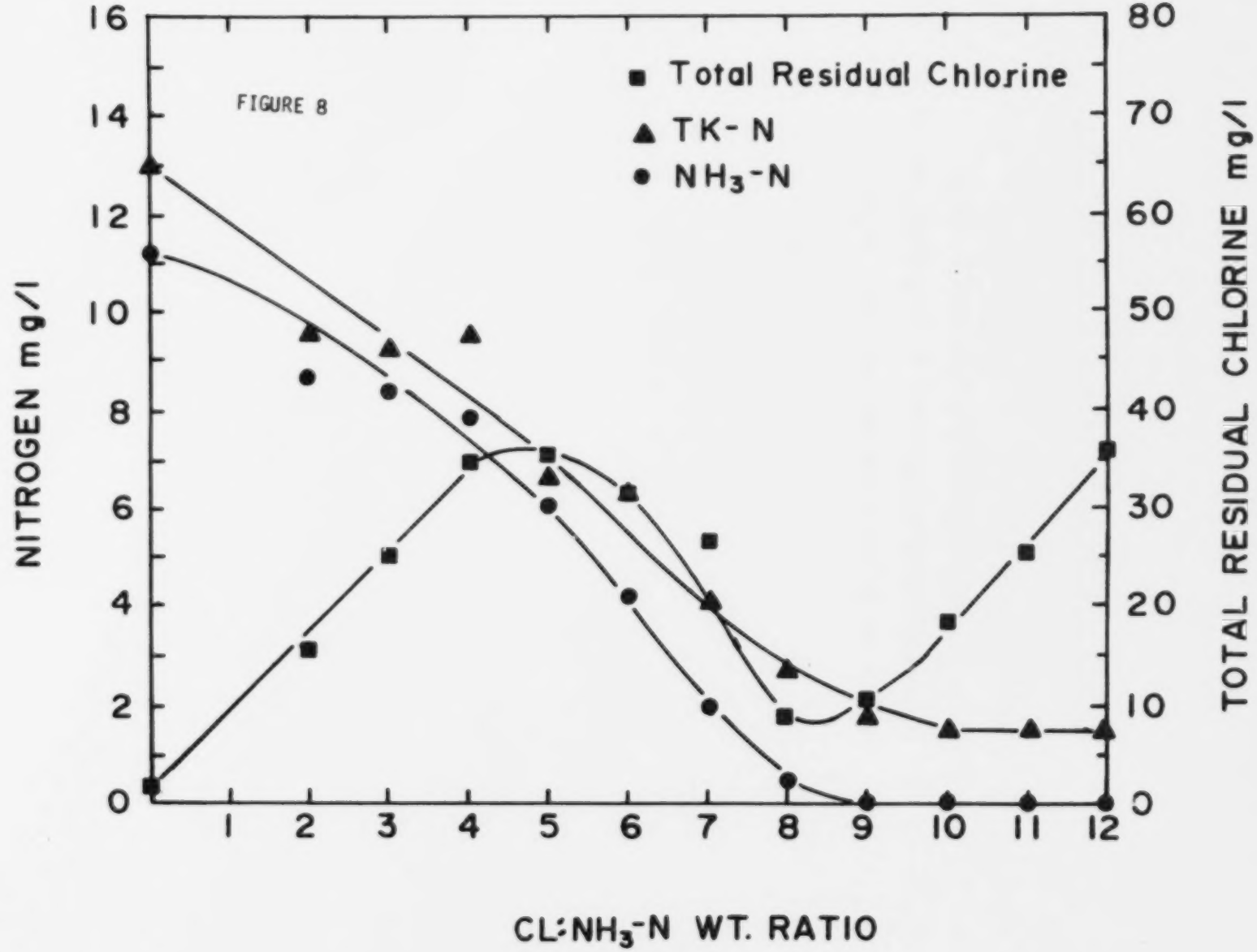
Total Residual Chlorine
TK-N
NH_3-N
NITROGEN mg/l
TOTAL RESIDUAL CHLORINE mg/l
CL:NH_3-N WT. RATIO
0
2
4
6
8
10
12
14
16
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9
10
11
12

Figure 9 - NITROGEN TRICHLORIDE AND NITRATE FORMATION DURING THE CHLORINATION OF LIME CLARIFIED AND FILTERED RAW WASTEWATER

Temperature = 23°C; NH_3-N = 11.2 mg/l; Suspended Solids = 4 mg/l; Total Alkalinity = 84 mg/l $CaCO_3$; pH Range During Chlorination = 6.5 - 7-5; Breakpoint between the 8:1 and 9:1 weight ratio of Cl:NH_3-N.

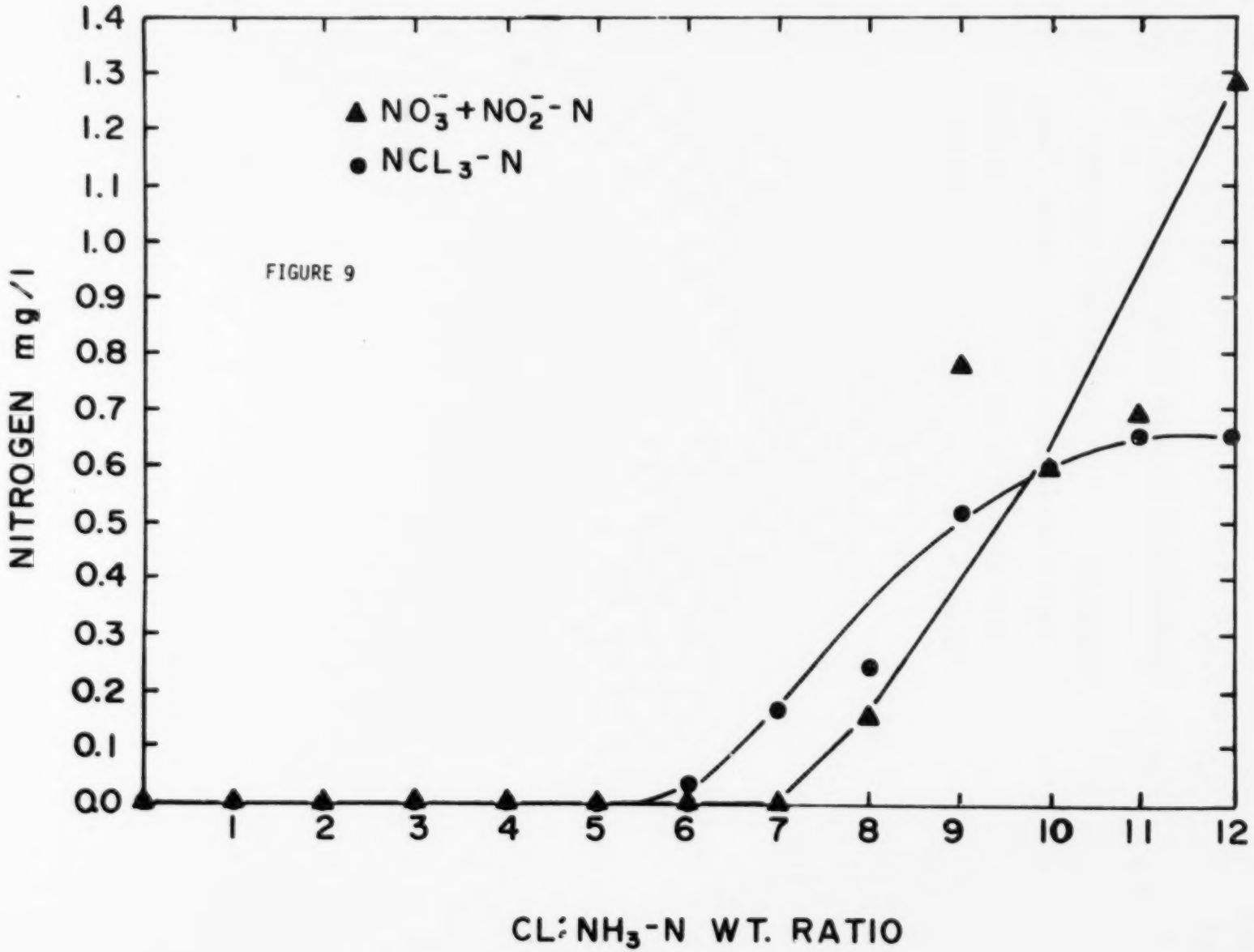
▲ $NO_3^- + NO_2^-$ - N
● NCL_3 - N
NITROGEN mg/l
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1
2
3
4
5
6
7
8
9
10
11
12
CL: NH_3-N WT. RATIO

FIGURE 9

Figure 10 - CHLORINATION OF SECONDARY EFFLUENT

Temperature = 22°C; NH_3-N = 8.1 mg/l; Suspended Solids = 40 mg/l; Total Alkalinity = 90 mg/l $CaCO_3$; pH Range During Chlorination = 6.5 - 7.5; Breakpoint between the 8:1 and 9:1 weight ratio of Cl:NH_3-N.

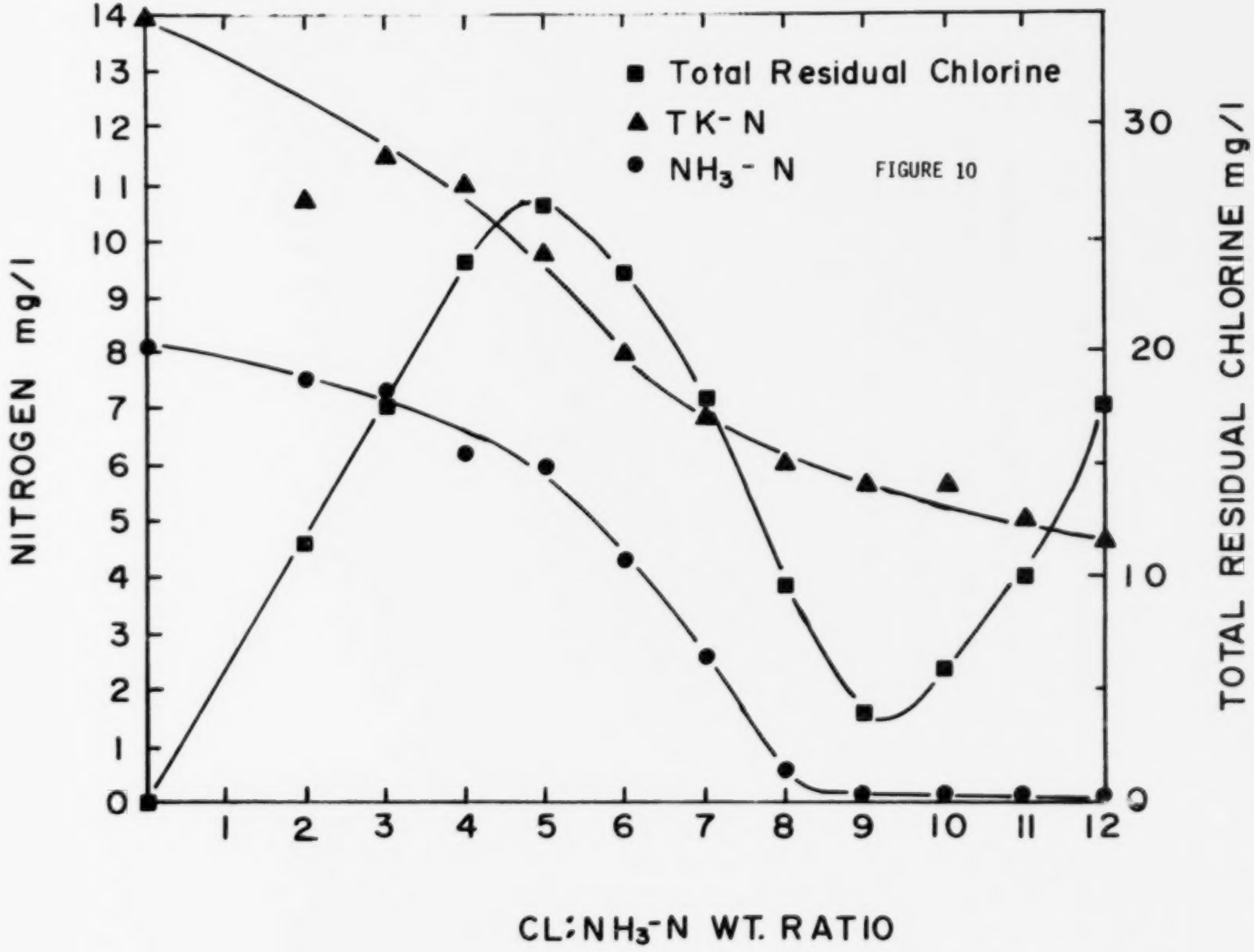
Total Residual Chlorine
TK-N
NH3-N
NITROGEN mg/l
TOTAL RESIDUAL CHLORINE mg/l
CL:NH3-N WT. RATIO
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
10
20
30

FIGURE 10

Figure 11 - NITROGEN TRICHLORIDE AND NITRATE FORMATION DURING THE CHLORINATION OF SECONDARY EFFLUENT

Temperature = 22°C; NH_3-N = 8.1 mg/l; Suspended Solids = 40 mg/l; Total Alkalinity = 90 mg/l $CaCO_3$; pH Range During Chlorination = 6.5 - 7.5; Breakpoint between the 8:1 and 9:1 weight ratio of Cl: NH_3-N.

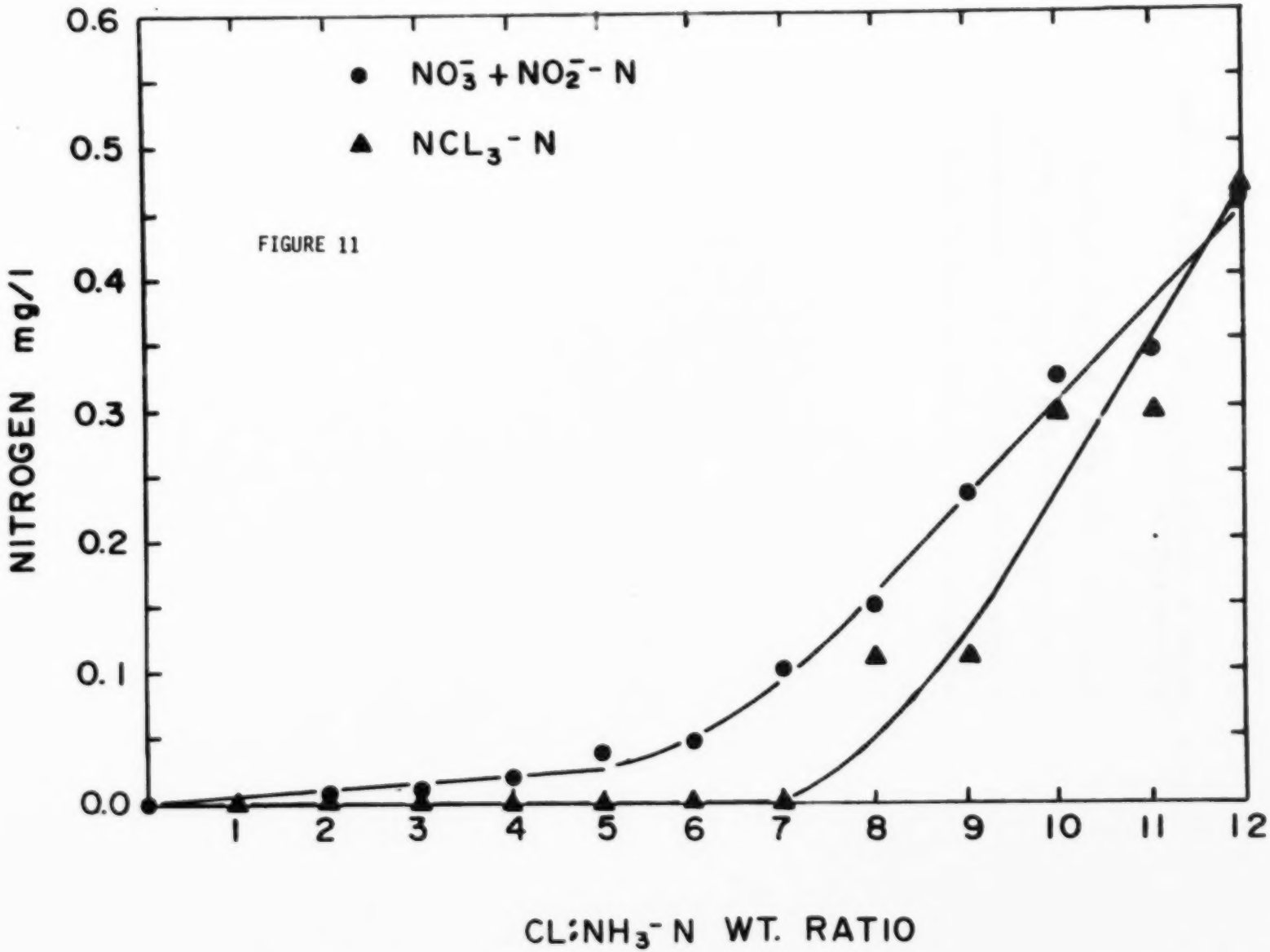
0.6
0.5
0.4
0.3
0.2
0.1
0.0
NITROGEN mg/l
$NO_3^- + NO_2^-$ - N
NCL_3 - N
1
2
3
4
5
6
7
8
9
10
11
12
CL:NH_3 - N WT. RATIO

FIGURE 11

Figure 12 - BREAKPOINT CHLORINATION OF LIME CLARIFIED AND FILTERED SECONDARY EFFLUENT

Temperature = 23°C; NH_3-N = 9.2 mg/l; Suspended Solids = 4 mg/l; Total Alkalinity = 84 mg/l $CaCO_3$; pH Range During Chlorination = 6.5 - 7.5; Breakpoint between the 7:1 and 8:1 weight ratio of Cl:NH_3-N.

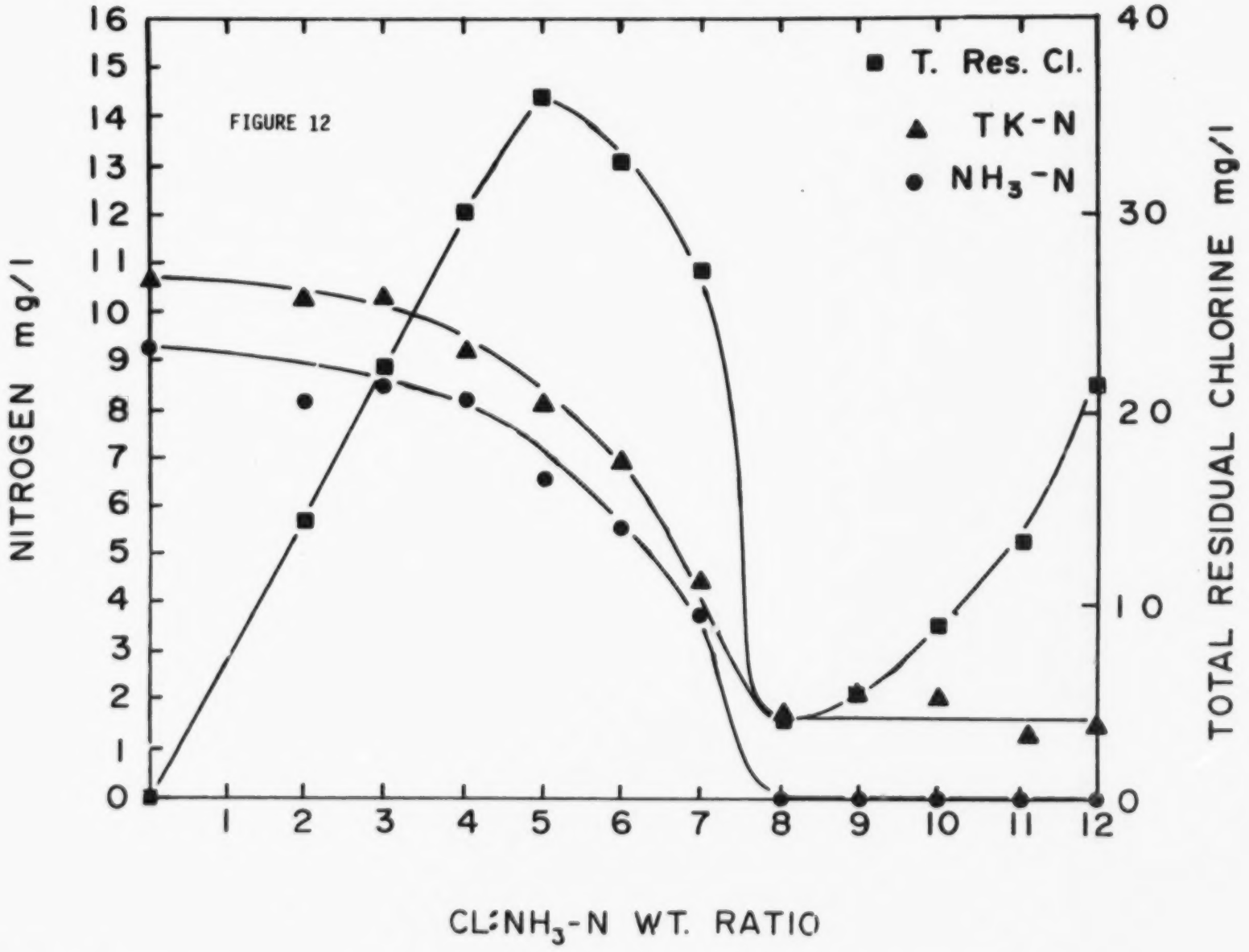
FIGURE 12
T. Res. Cl.
TK-N
NH3-N
NITROGEN mg/l
TOTAL RESIDUAL CHLORINE mg/l
CL:NH3-N WT. RATIO
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
20
30
40

Figure 13 - NITROGEN TRICHLORIDE AND NITRATE FORMATION DURING CHLORINATION OF LIME CLARIFIED AND FILTERED SECONDARY EFFLUENT

Temperature - 23°C; NH_3-4 = 9.2 mg/l; Suspended Solids = 4 mg/l; Total Alkalinity = 84 mg/l $CaCO_3$; pH Range During Chlorination = 6.5 - 7.5; Breakpoint between the 7:1 and 8:1 weight ratio of Cl:NH_3-N.

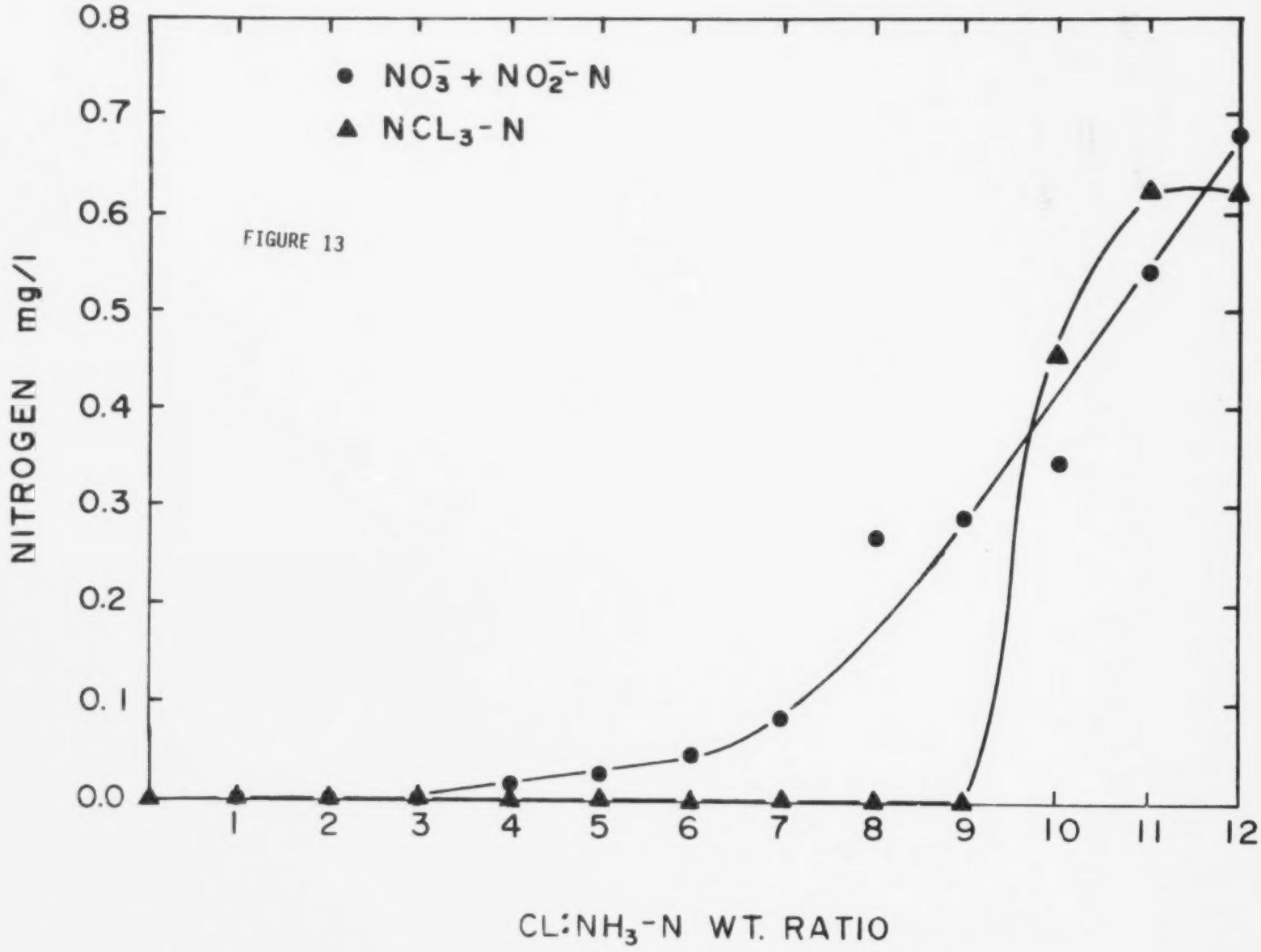
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
NITROGEN mg/l
● $NO_3^- + NO_2^-$-N
▲ NCL_3-N
1
2
3
4
5
6
7
8
9
10
11
12
CL:NH_3-N WT. RATIO

FIGURE 13